4.1 Introduction

Ion bombardment induced effect and structural modification of solids have been studied from decades [Audouard 88, Klaumünzer 83]. Apart from these studies, some ion induced directional effects are also recognized. These are Frenkel pairs (vacancy-interstitial pair) creation and their separation [Kinchin 55], sputtering, and macroscopic effects like "Klaumünzer effect [Klaumünzer 83]" (widening and flattening of amorphous solids in direction perpendicular to the ion beam). Furthermore, a lateral mass transport at the surface of the solid was observed [Chicoiné 97], which consists of transport of matter on the irradiated surface in the direction of component of ion velocity parallel to the surface. The phenomenon was observed at the boundary between the irradiated and unirradiated zone of the sample surface. There are two schools of thought to explain this phenomenon. In the first one, macroscopic momentum transfer to the irradiated solid by ion beam was
considered as the mechanism \[\text{Cliché 95}\]. Here macroscopic momentum transfer means that the ion momentum is transferred to a macroscopic amount of material as a whole, such as entire ion track or surface layer rather than to a single atom \[\text{Roorda 95}\]. The microscopic momentum transfer plays a role in creating point defects such as Frenkel pairs but the mass transport (~0.4 \(\mu m\), parallel to the surface) effect is too big to be caused by direct microscopic momentum transfer. In the second one, the concept such as thermal widening of the cylindrical damaged zone caused by lateral stress due to SHI irradiation has been invoked to explain the mass transport at the surface. The directional effects were explained on the basis of viscoelastic model\(^1\).

In this chapter a detailed quantitative investigation of lateral mass transport (LMT) phenomenon on 200 \(MeV\) \(^{107}\)Ag\(^{+}\) irradiated Si(111) and InP(111) surfaces has been performed using atomic force microscopy (AFM) and X-ray diffraction (XRD) techniques. The AFM topographies showed the directional effects of ion beam on the morphology of the resulting non-equilibrium surfaces that depend on the ion fluence. A new type of ditch and dike structure was observed \[\text{Singh 2000c, 2001a}\] on passivated silicon surfaces after ion bombardment. In another experiment, these structures were found at the chemically grown terraces of Si surfaces after irradiation. These structures are different from the previously observed ditch and dike structures, which were found at the boundary \[\text{Chivine 97}\] between the irradiated and unirradiated zones. These structures may be of technological importance, since these structures are of nano size in height. The fluence dependence of the mass transport is attributed to the cumulative effect of ion irradiation arising due to the overlapping of ion induced damaged zones and electronic excitation induced shear motion of atoms towards the surface. These structures were distributed over the irradiated surface. The power spectral density (PSD) analysis of irradiated surface showed that the diffusion is the dominant mechanism in the evolution of surface under SHI bombardment, which agrees well with the LMT process observed by AFM in real space.

4.2 Experiment

To understand the mechanism of lateral mass transport in detail, we have performed three independent experiments using wafers of <111> oriented n-type (P doped) Si and semi-

\(^1\) Details on momentum transfer and viscoelastic model are discussed in Chapter 1.
insulating InP single crystals procured from MTI, USA. All of the samples were irradiated by 200 MeV Ag\(^{14}\) ions available from Pelletron accelerator [Kanjilal 93] at Nuclear Science Centre. The irradiation was performed at 15° angle with respect to the surface normal. Ion beam was scanned over 10\(\times\)10 mm\(^2\) area on sample surface by a magnetic scanner for uniform irradiation. The area of scan was optimized by directly monitoring the movement of the beam on a calibrated quartz specimen using a CCD camera fixed to a forward view port of the experimental chamber. On top of the target a stainless steel mask was clamped, with a 5\(\times\)5 mm\(^2\) rectangular opening through which the ions could hit the sample surface. The thickness of all of the samples was 0.5 mm. During irradiation the temperature of the samples was maintained at 80 K. The chamber pressure during irradiation was maintained at 7\(\times\)10\(^{-7}\) mbar using cryo-pump for reducing the hydrocarbon contamination in the chamber. The samples were irradiated with flunkies varying between 10\(^{12}\) to 10\(^{14}\) ions cm\(^{-2}\). The ion flux was 10\(^9\) ions cm\(^{-2}\) s\(^{-1}\). Flunkies were determined by integrating the charges of the ions falling on the sample directly by a current integrator. The secondary electrons were suppressed by a negatively biased (-120 Volt) cylindrical suppressor assembly, which encloses the sample holder. The beam enters inside the suppressor through an aperture in front of the sample. Ion fluence is estimated within an accuracy of \(\pm\) 5%.

In first and second irradiation experiments with Si samples, all of the above experimental conditions were same except the chemical treatment of the surface before the irradiation. In the first experiment, prior to mounting of samples on the target ladder for irradiation chemical cleaning and hydrogen passivation of Si samples were carried out.\(^2\) Scanning tunneling spectroscopy was performed on one of the samples and no oxygen related gap states were found as shown in Figure 4.1. This shows that Si surfaces were really passivated. In the second experiment, the Si surfaces were etched in NH\(_4\)F solution for longer duration. This chemical treatment of the Si surfaces results in hydrogen passivated trapezoid shaped terraces uniformly distributed over the entire surface [Singh 2001a]. In the third experiment, InP(111) surfaces were degreased with acetone and trichloroethyelene solutions prior to mounting on the target ladder for irradiation. All the chemicals used were of electronic grade. In all experiments, one of the

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\(^2\)Chemical cleaning and hydrogen passivation of Si surface are given in Chapter 2, section 2.2.
samples was left unirradiated on the target ladder and was used as the pristine (reference) sample. This is to ensure that effect is purely due to ion irradiation and is not an artifact.

Figure 4.1 The variation of electronic density of states $\rho(E)$ of hydrogen passivated n-Si(111) measured by scanning tunnelling spectroscopy. The curve does not show any oxygen-related peaks.

Figure 4.2 AFM image of 1x1 $\mu m^2$ gold grid structures on Si surface used for calibration purpose.

The sample surfaces were analyzed using AFM from digital instruments (Nanoscope III) by Si$_3$N$_4$ tips. A typical scan area was about 1x1$\mu$m$^2$. All samples were scanned in trace and retrace directions. This was done to identify the possible direction
induced scanning artifacts. The AFM calibration was accomplished by imaging a gold micro grid structure on Si surface (see Figure 4.2) before each set of the experiments. XRD measurements were performed using Cu Kα X-ray ($\lambda = 1.54 \, \text{Å}$) for Si(111) and Mo Kα X-ray ($\lambda = 0.71 \, \text{Å}$) for InP(111) samples.

![AFM pictures](image)

**Figure 4.3** AFM pictures of hydrogen passivated Si(111) surfaces (a) pristine sample, (b) irradiated by 200 MeV Ag$^{+14}$ ions at the fluence of $10^{13}$, (c) $5 \times 10^{13}$ and (d) $10^{14}$ ions cm$^{-2}$. 
4.3 Results for silicon: formation of ditch and dike structure

The AFM pictures of hydrogen passivated Si wafers irradiated by 200 MeV Ag$^{+14}$ ions at various fluences are shown in Figure 4.3. The effect of irradiation on the surface is visible from the change in the surface morphology at different ion fluencies. The root mean square (RMS) values of surface roughness show a super linear increase with ion fluence as shown in Figure 4.4.

![Figure 4.4](image)

**Figure 4.4** The superlinear variation of RMS surface roughness $\sigma$ with fluence $\phi$ by irradiation with 200 MeV $^{107}$Ag$^{+14}$ ions. The roughness was estimated by AFM height data as an averaged over 10 different places on the surface.

A new type of ditch and dike structure was observed [Singh 2000c] on the sample surface at $5\times10^{13}$ ions cm$^{-2}$ fluence. The AFM pictures of these structures are shown in Figure 4.5 and Figure 4.6 with a line profile along one of the ditch and dike structure. The average depth of ditch is 25 nm and width is 0.6 $\mu$m. The dike, which followed the ditch has height of 22.6 nm and width of 0.7 $\mu$m. These structures are different from the previously observed ditch and dike structures [Chicoine 97] on an amorphous Si and InP surfaces using 24 MeV Se ions. In their study, an implantation mask was used to create a boundary between the irradiated and unirradiated regions. The ditch and dike structures were observed at the boundary of irradiated and unirradiated regions with ditch occurring at one side of the boundary and dike at the opposite side of the implantation mask. Further, the ditch and dike structures were separated by several hundreds of $\mu$m.
Figure 4.5 The AFM picture of Si (111) surface irradiated by 200 MeV Ag$^{+14}$ ion at 15° angle of incidence with respect to surface normal at a fluence of $5\times10^{13}$ ions cm$^{-2}$ showing (a) ditch and dike structures and (b) line profile along one of these structures.
Figure 4.6 The AFM pictures of Si(111) surface irradiated by 200 MeV Ag$^{+4}$ ions at 15° angle of incidence with respect to surface normal at fluence of $5 \times 10^{13}$ ions cm$^{-2}$ showing ditch and dike structures (a) 3-D view and (b) 2-D view of different portion of the image.
In the present observation, however, the ditch and dike structures were found on the irradiated surface and each ditch is followed by a dike structure. These structures are distributed over the surface. All the dikes were formed on the same side of the ditch. This is in contrast to the result observed by Biró and co-workers [Biró 96] where the ion-induced craters were symmetrically surrounded by piled material. The number of these structures does not match with the ion fluence. This indicates that the effect is cumulative in nature. It is formed by overlapping of ion induced damage zones. XRD spectra of irradiated surfaces are shown in Figure 4.7.

![Figure 4.7 XRD spectra of hydrogen passivated Si(111) surfaces: (a) pristine sample, (b) and (c) samples irradiated by 200 MeV $^{107}$Ag$^{14}$ ions at fluence of $10^{13}$ and $5 \times 10^{13}$ ions cm$^{-2}$ respectively.](image)

The Si(111) peak at 2θ value of 28.4° is visible in the spectra. After $1 \times 10^{13}$ ions cm$^{-2}$ fluence the peak intensity decreases and at $5 \times 10^{13}$ ions cm$^{-2}$ the intensity of the peak
reduced to 0.2% of the pristine value. This shows the amorphization of the surface after irradiation.

In the second experiment, the trapezoid shaped terraces were observed on n-type Si(111) surfaces after the prolonged etching in 40% NH₄F solution as shown in Figure 4.8. These trapezoid terraces were distributed over the Si surface. Thanh et al. [Thanh 2000] investigated the surface structure and chemistry of Si surfaces after wet chemical etching in HF and NH₄F solutions. The results suggested that hydrogen passivated (111) facets were formed on Si surfaces only after a prolonged etching in NH₄F solution and they remained stable up to an annealing temperature of 650°C. In the present case, the observed terraces are having atomically flat surface and smooth facets, whereas other regions are rather rough. These atomically flat trapezoid terraces can be a place to observe the ion beam induced mass transport on the surface.

Figure 4.8 AFM topographs showing terrace growth on hydrogen passivated Si(111) surface after prolonged etching in 40% NH₄F solution.

The LMT on these chemically grown terraces after 200 MeV Ag⁺ ions irradiation at 15° angle with respect to the surface normal for fluence varying from 10^{12} to 10^{14} ions cm⁻² is systematically presented in Figure 4.9. The direction of the incident ions is also depicted. A dike structure was observed at the boundary of the terrace.
Figure 4.9 AFM line profiles showing the lateral mass transport on the terraces of hydrogen passivated Si(111) surfaces (a) pristine and irradiated by 200 MeV $^{107}$Ag$^{+14}$ ions at 15° angle with respect to surface normal at the fluence of (b) $10^{12}$, (c) $5 \times 10^{12}$, (d) $10^{13}$, (e) $5 \times 10^{13}$ and (f) $10^{14}$ ions cm$^{-2}$. 
All such dikes were formed in the same side of the incident ion beam. The height of dike structure \( h \) and number of displaced atoms \( N \) on the terrace forming the dike structure with varying fluences are given in Table 4.1.

### Table 4.1

<table>
<thead>
<tr>
<th>Fluence (ions cm(^{-2}))</th>
<th>( h ) [nm]</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( 5 \times 10^{12} )</td>
<td>17.3</td>
<td>7.3\times10^6</td>
</tr>
<tr>
<td>( 10^{13} )</td>
<td>21.1</td>
<td>6.6\times10^6</td>
</tr>
<tr>
<td>( 5 \times 10^{13} )</td>
<td>15.8</td>
<td>1.2\times10^7</td>
</tr>
<tr>
<td>( 10^{14} )</td>
<td>5.2</td>
<td>4.5\times10^6</td>
</tr>
</tbody>
</table>

Table 4.1 The height of dike structure \( h \) and number of displaced atoms \( N \) at the terrace boundary forming the dike structure after 200 MeV Ag\(^{14}\) ions irradiation on Si(111) surfaces as a function of fluence.

![AFM pictures of semi-insulating InP(111) surfaces](image)

Figure 4.10 AFM pictures of semi-insulating InP(111) surfaces (a) pristine sample, (b) irradiated by 200 MeV Ag\(^{14}\) ions at the fluence of \( 5 \times 10^{12} \), (c) \( 5 \times 10^{13} \) and (d) \( 10^{14} \) ions cm\(^{-2}\).
4.4 Results for InP: formation of step structure

The evolution of the surface morphology of InP(111) wafers irradiated by 200 MeV $^{107}$Ag$^{+14}$ ions at fluxes ranging from $10^{12}$ to $10^{14}$ ions cm$^{-2}$ is shown in Figure 4.10. One of the prominent features seen through the AFM pictures is the development of a rough surface with ion fluence. The root mean square surface roughness $\sigma$ evaluated from the AFM data varies with fluence as shown in Figure 4.11. Error bar is put according to the standard deviation in roughness values at various places.

![Figure 4.11](image)

**Figure 4.11** The variation of RMS surface roughness $\sigma$ with fluence $\phi$ of 200 MeV $^{107}$Ag$^{+14}$ ions irradiated InP(111) surfaces. The roughness was estimated by AFM height data as an averaged over 10 different places on the surface.

A step structure (see Figure 4.12) develops at the mask boundary between the irradiated and unirradiated regions after the ion bombardment. The direction of the ion beam is depicted in the figure. The height corresponding to the step structure was found to be 103 nm. The InP compacts after the ion irradiation due to increase in density after irradiation [Cliché 94]. The present AFM measurements were performed about 15 days after the irradiation. From the structural relaxation of irradiated InP, it is expected that during this time almost all the density relaxation has occurred. Hence, the observed step structure at the boundary between irradiated and unirradiated regions cannot be explained by density changes alone. One needs to consider the viscous flow of matter at the surface to explain such features.
Figure 4.12 AFM topographs showing lateral mass transport at (a) mask boundary induced by 200 MeV Ag$^{14+}$ ions at 15° angle of incidence with respect to surface normal at a fluence of $10^{14}$ ions cm$^{-2}$ (b) line profile along the step structure.
The XRD [Mo $K_a$] spectra of irradiated InP(111) surfaces are shown in Figure 4.13. The intensity of $<111>$ peak at 20 value of 12.21° decreases with fluence and it reduced to 21% at the fluence of $10^{14}$ ions cm$^{-2}$. The reduction in peak intensity and increase in the full width at half maximum (FWHM) to 180% indicate the amorphization of the surface layers of crystalline InP after irradiation.

![XRD spectra of InP(111) surfaces](image)

**Figure 4.13** XRD spectra of InP(111) surfaces: (a) pristine sample and samples irradiated by 200 MeV $^{107}$Ag$^{+14}$ ions at the fluences of (b) $10^{12}$, (c) $5 \times 10^{13}$, and (d) $10^{14}$ ions cm$^{-2}$ respectively.

### 4.5 Lateral mass transport mechanism

The formation of ditch and dike structures on the irradiated Si surfaces or the step structure at the boundary between the irradiated and unirradiated regions are due to the ion-induced lateral mass transport on the surface. The lateral mass transport phenomenon consists of the displacement of the irradiated material along the surface in the direction of...
the ion velocity parallel to the surface. This phenomenon occurs only in amorphous material [Cliché 95, Klaumunzer 83]. In case of crystalline materials, it becomes apparent only after the material becomes amorphized. Let us first discuss the amorphization of crystalline Si and InP by SHI irradiation.

4.5.1 Swift heavy ion induced amorphization

We will discuss this in two different cases (i) low fluence regime ($\phi < \phi_c$, where $\phi_c$ is the critical fluence where the damage zones start overlapping) and (ii) high fluence regime ($\phi > \phi_c$), where the damage zones overlap with each other.

Case (i): $\phi < \phi_c$

In this case of low fluence regime of ion irradiation, the damaged regions do not overlap with each other. The total damage increases with fluence linearly. After some value of fluence damage zones start overlapping. Earlier experiments [Levalois 92] involving giga electron volts (GeV) energies have proved that it is not possible to create amorphized latent tracks in bulk silicon by mono-atomic ions (such as Au, Ag, I etc.). There is a threshold value ($S_e$)$_{th}$ ($\sim 30$ keV/nm) of the electronic energy loss $S_e$ for the creation of amorphized latent tracks in the crystalline Si [Canut 98]. In the present case of irradiation of Si by 200 MeV Ag$^{+14}$ ion the values of $S_e$ and $S_n$ are 12.56 keV/nm and 33.5 eV/nm respectively as estimated by SRIM code [Ziegler 85]. In present case, $S_e < (S_e)_{th}$ so the amorphized latent track formation in bulk silicon single crystal is not expected. Tracks in crystalline silicon can only be created by high energy cluster ions of MeV range C$_{60}$ ions [Dunlop 98] which leads to the confinement of large energy density in a localized region exceeding the ($S_e$)$_{th}$ value. We address a question: why does such a large ($S_e$)$_{th}$ ($\sim 30$ keV/nm) is required in case of creation of amorphized latent tracks in crystalline Si? In this regard it is very interesting to note that amorphization does occur when crystalline Si is irradiated with fs laser pulses [Tom 88]. Moreover, the absorbed energy density from heavy ion exceeds by a factor of 5-10 compared to that absorbed from laser pulses (by considering the equivalent volumes). This is due to the fact that the excitation of electrons with laser pulses is more coherent in the sense that the excited electrons occupy energy levels not having a large spread. Whereas, in case of SHI irradiation, spreading of energy
levels is very large and the electron diffusivity is also governed by ballistic events, which
do not favor the thermal energy localization necessary for lattice melting \cite{Miotello 97}. Hence, ballistic events impede the melting of the track created by the impact of single ion in crystalline Si.

The surface however presents a different scenario. In a highly localized region of a few \textit{nm} around the ion path the surface can be amorphized. The earlier observations showed that \textit{MeV} heavy ions can generate latent tracks in thin metallic film \cite{Merkle 62} whereas using the same projectile ion no damage was generated in bulk samples. During ion irradiation of the Si surface hydrogen atoms desorb from the passivated Si surface sites. This hydrogen desorption induces surface states and thus leaves unsaturated dangling bonds on the surface. By considering the ion interaction zone of 5 \textit{nm} diameter on Si surface \cite{Toulemonde 92} these dangling bonds with cohesive energy per bond of 2.32 \textit{eV} would add approximately 0.25 \textit{keV} energy to the interaction zone of the surface. This extra energy on the surface of the interaction zone makes it active and facilitates surface modifications. It has been shown that point defects such as broken bonds created by incident ion lead to the radiation enhanced flow in the amorphous materials \cite{Volkert 91, Witvrouw 93}. With certain amount of disorder induced by SHI on the Si surface in the form of broken bonds, these active regions become sensitive to the irradiation. The unsaturated dangling bonds on the surface may present a driving force for the mass flow to occur, so that the Si atoms get passivated. These displaced Si atoms, while saturating the surface dangling bonds may create more dangling bonds. This makes the driving force for the atomic motion towards the surface even stronger. The process thus evolves with a positive feed back effect. The large increase in the surface roughness \textit{(see Figure 4.4)} from 0.96 \textit{nm} in the reference sample to the 18.33 \textit{nm} in sample irradiated at a fluence of 5x10^{13} \textit{ions cm}^{-2} fluence is a consequence of this positive feed back effect \cite{Singh 2000c}. Therefore, SHI irradiation may produce surface amorphization without affecting bulk. The irradiation of InP surface with 200 \textit{MeV}^{107}Ag^{+14} ions is an interesting case. The values of $S_e$ and $S_n$ are 16.6 and 0.05 \textit{keV/nm} respectively as estimated by SRIM \cite{Ziegler 85}. The threshold value \textit{(S_e)_{th}} for the creation of amorphized latent tracks in the crystalline InP \cite{Herre 98} is 13 \textit{keV/nm}. In present case, $S_e > (S_e)_{th}$ so the amorphized latent track formation in bulk InP single crystal is expected. Thus, in this case surface as well as bulk are expected to amorphized.
Case (ii): $\phi > \phi_c$

In this case, the damaged regions overlap with each other. In the analysis of SHI induced modifications in materials, it is assumed that the amorphized zone created due to passage of the ion does not get further modified when another ion passes through the same zone [Dufour 99]. Based on this assumption, it is possible to estimate the ion track radius from Poisson's formula. Considering 5 nm as the diameter of the modified zone on Si surface due to single ion impact [Toulemonde 92], it can be estimated that the total surface gets covered with damaged zones at a critical fluence of $10^{12}$ ions cm$^{-2}$.\footnote{With an effective ion interaction zone of 5 nm in diameter the critical fluence required to cover the surface area of 1cm$^2$ is $\frac{1cm^2}{\pi(5nm)^2} \sim 10^{12}$ ions cm$^{-2}$.} According to the analysis of Dufour et al. which has been successfully applied to metals and even to some insulators [Dufour 97, Toulemonde 94] it is expected that beyond the critical fluence, no further materials modification should occur on the surfaces of Si and InP due to SHI irradiation. The Si and InP surfaces however shows a dramatic surface modification beyond the critical fluence (Figure 4.3 and Figure 4.10 respectively). Therefore, the interaction between damaged zones which has been neglected in case of metals [Dufour 97,99] and in some insulators [Toulemonde 94] plays a very significant role in bringing about surface modification in semiconductors like silicon and InP under SHI irradiation. At around a critical fluence $\phi_c$, surface get amorphized and an amorphous/crystalline (a/c) interface is created. The extent of amorphization in a region on the surface is proportional to the number of ions hitting that region. The thickness of the amorphized layer in that region is therefore expected to scale with this multiple-ion hit process. Ion beam induced crystallization and amorphization at a/c interface in Si has been studied by X-TEM technique [Leiberich 87]. They studied the interface dynamics during 1.5 MeV Xe ion irradiation. Free energy of the amorphous phase in Si is above that of the crystalline phase by 0.12 eV per atom [Chiarotti 92]. So the amorphization of crystalline Si needs some extra defect energy. The interfacial growth at given temperature and irradiation conditions is controlled by the density of defect complexes. The density of defect complexes determines the contribution, which the defect free energy makes to the total free energy of the system. The density of defect complexes depends on the overlapping of the damaged
zones or it scales with the multiple-ions hit probability. Thus, if the defect free energy is high enough, the total free energy of the defect laced crystalline side of the a/c interface may actually exceed the free energy of the amorphous phase and the a/c interface moves towards the crystalline side. This emphasizes the role of overlapping of damaged zones in the dynamics of a/c interface. The amorphous Si material is produced if the energy deposition per unit volume reaches a level of \(6 \times 10^{20} \text{ keV cm}^{-3}\) [Chiarotti 92]. The energy density deposited by 200 MeV Ag\(^{+14}\) ion in Si is \(1.61 \times 10^{20} \text{ keV cm}^{-3}\). So, for the amorphization of Si the number of tracks to be overlap will be about 4. Hence, the ion fluence \(\phi \geq 4\phi_c\) is needed for the amorphization and dynamics of a/c interface layer towards the crystalline side [Singh 2001a]. It is also observed experimentally that amorphization starts (see Figure 4.7) after the fluence of \(5 \times 10^{12} \text{ ions cm}^{-2}\). The drastic decrease of Si(111) XRD peak at 2\(\theta\) value of 28.4° with increasing fluence (see Figure 4.7) indicates that the top surface is completely amorphized. The amorphized layer attenuates the intensity of XRD peak corresponding to its thickness measured from the irradiated surface. The attenuated line without much increase in its width thus corresponds to the undamaged crystalline structure underneath the amorphous over layer. Therefore, SHI irradiation induces surface modification in Si without affecting its bulk along the ion trajectory.

The critical energy density \(E_c\) for amorphization (\(\sim 2.5 \times 10^{20} \text{ keV/cm}^3\)) in case of III-V semiconductor is lower than that of Si (\(\sim 6 \times 10^{21} \text{ keV cm}^3\)). This is due to the fact that the compound semiconductor lattice contains different atoms in the basis. This makes the contribution in the form of configurational entropy and lowers the free energy. In the present case of irradiation of InP by 200 MeV \(^{107}\text{Ag}^{+14}\) ion, the values of \(S_e\) and \(S_n\) are 16.47 and 0.05 \(\text{keV/nnm}\), respectively, as estimated by SRIM. The energy density deposited by 200 MeV \(^{107}\text{Ag}^{+14}\) ion on InP surface is \(\sim 2.1 \times 10^{20} \text{ keV/cm}^3\) (by assuming 10 nm as track diameter) which is of the same order as the \(E_c\) for amorphization. Therefore, a single ion impact can create an amorphized latent track. In fact, Herre et al. observed the formation of tracks in InP after irradiation of 250 MeV Xe ions at room temperature [Herre 98]. The \((S_e)_{\text{th}}\) was estimated as 13 \(\text{keV/nnm}\), which is small compared to the \(S_e\) (16.47 \(\text{keV/nnm}\)) of 200 MeV Ag\(^{+14}\) ions in InP. At low temperature the continuous latent tracks were not observed but small damage and damage cluster have been seen [Gaiduk
Each ion however creates a damage region on the surface. At around the critical fluence $\phi_c$, amorphized zones due to single ion impact overlap. The total surface get amorphized and an a/c interface is created inside the sample. The drastic decrease of InP(111) XRD peak at 2$\theta$ value of 12.21° with increasing ion fluence (see Figure 4.13) indicates that top surface is amorphized. The a/c interface layer can influence the surface morphology when the amorphous layer becomes viscous and flows under momentum transfer induced by SHI irradiation. The schematic diagram of SHI irradiation induced amorphization and creation of a/c interface are shown in Figure 4.14. Because of the multiple-ions hit probability the a/c interface is not smooth.

**4.5.2 Ditch and dike formation**

The location of the ditch and dike with respect to the direction of ion beam points to the applicability of a momentum transfer model [Cliche 95]. The ion beam at 15° angle of incidence with respect to surface normal has a lateral momentum component along the surface. This can lead to mass transport from ditch to dike. The momentum transfer mechanism, however, does not explain the following two distinctive features of presently observed ditch and dike structures: (1) lack of a flat region between ditch and dike structures and (2) appearance of large number of ditch and dike pairs. The number of such structures is much smaller than the ion fluence used.

To understand this new type of ditch and dike structure, we note that beyond a critical fluence, the damaged zones are expected to overlap with each other. The extent of amorphization in a region on the surface is proportional to the number of ions hitting that region. The thickness of the amorphized layer in that region therefore is expected to scale with this multiple-ion hit process. Its probability will increase with increasing ion fluence beyond the critical fluence. At $5 \times 10^{13}$ ions cm$^{-2}$ fluence, which is 50 times higher than the critical fluence, a significant number of ions will participate in multiple-ions hit process. The thickness of the amorphized layer was estimated by the comparison of $S_e$'s, fluence and thickness of the amorphized layer of previously observed data of 30 MeV Se ions in Si. The range of the 200 MeV Ag ion in Si is 22.3 $\mu$m compared to the thickness $d$ 6.4 $\mu$m of the amorphized layer.
Figure 4.14 Schematic diagram showing (a) the formation of amorphized surface zone due to the single ion impact for $S_x < S_{eth}$ and (b) amorphized latent tracks for $S_x > S_{eth}$ and the creation of amorphous/crystalline (a/c) interface for $S_x < S_{eth}$ and at the fluence greater than the fluence required for overlapping of the damaged zones.
This process being statistical would introduce fluctuations in the thickness of amorphized layer over the crystalline medium as measured from the irradiated surface. Hence, the amount of amorphous material beneath the irradiation surface varies from region to region. This situation is very different from that of SHI induced modification in metals and insulators in the low fluence regime, where the evolution of the system with ion fluence is considered only in xy-plane [Dufour 97,99]. In high fluence regime, where tracks are not formed but surface is amorphized as in the present case the system evolution along the z-axis, i.e. along the surface normal inside the material become important. The SHI induced mass transport arising either due to viscoelastic behavior [Trinkaus 95] of the material or due to momentum transfer [Cliché 95] is a phenomenon seen only in amorphous materials. The depth of the amorphous layer therefore becomes a crucial parameter in mass transport phenomenon. In the regions of the sample where the depth of amorphized zone is large mass transport resulting due to either of the above mechanisms is also expected to be large. The interface layer between crystalline and amorphous region can influence the surface morphology when the amorphous layer becomes viscous and flows under momentum transfer induced by SHI irradiation. The radiation-induced decrease in viscosity reflects the uneven structure of the interface layer on the top surface and hence makes this uneven structure behave like an internal mask.
[see Figure 4.15]. The momentum provided by the incidence ions produce anisotropy in the dike structure with respect to the ditch. The number of such internal masks determines the number of ditch and dike structures and will be dictated by the probability of multiple-ion hit phenomenon as discussed earlier.

The component of the force parallel to the surface gives shear stress to the material. The formation of step structure (see Figure 4.12) at the mask boundary between the irradiated and unirradiated regions is the result of viscous flow of this amorphized layer over the crystalline interface. The position of the step structure with respect to the beam direction points to the applicability of momentum transfer model.

4.5.4 How does ion generate lateral stress within the ion track?

Let us see how a lateral stress gets generated within the track. Each ion deposits its energy along the track by inelastic scattering with electrons and elastic scattering with surrounding atoms. While traversing through the matter the charge neutralization process occurs and energy deposited near the surface is mainly coulomb energy. The instantaneous force applied by the ion can be assumed as gradient of Coulomb energy (equals to its energy loss) and varies with depth inside the matter measured from the irradiated surface. The component of the force parallel to the surface gives lateral velocity to the different layers of the material. The magnitude of the lateral stress (stress = force/area) is given by [Chicoine 97]:

\[ \tau_{la} = \frac{\sin \theta \cos \theta}{A} (S_e + S_n) \]  

where \( \theta \) is the incidence angle between the ion beam and the surface normal and \( A \) is the area of the ion track. For 200 MeV \(^{107}\)Ag\(^{+14}\) ions the stress in the implanted region is calculated as \( \sim 2.67 \times 10^8 \) N m\(^{-2}\), ion flux is \( 10^9 \) ions cm\(^{-2}\) s\(^{-1}\) and damaged circular region has a diameter of \( \sim 10 \) nm. This is equal to about \( 10^3 \) atmospheric pressure. This lateral stress causes the plastic flow of the material on the surface. The direction of the flow is provided by angular displacement of the ion beam with respect to the surface normal.

\(^4\) Detail of ion-solid interaction process is given in Chapter 1..  
\(^5\) Since, \( F = -VE \), where \( F \) is the force and \( E \) is the energy.
4.5.5 Why does amorphization important for mass flow?

In crystalline materials, if the deformed liquid track is re-crystallized by epitaxial growth it returns to its original form. While, it can be quenched in its deformed state in an amorphous material. The re-crystallization of the liquid track depends on the interface (between liquid track and solid surrounding) resolidification velocity. The resolidification velocity of liquid-solid interface in the case of Si(111) is 14-20 m/s with a cooling rate of $10^{11}$ K/s [Thompson 83]. This is independent of the way by which heat is transported away from the interface. When the resolidification velocity is lower than 14 m/s the melted region recrystallize by epitaxy and go back to its original form leaving behind high density of microscopic defects.

In a very interesting experiment of surface wave velocity measurements from Brillouin techniques [Bhadra 88], it has been shown that the elastic constants (as shear moduli) of Si changes only when the sample shows sign of becoming amorphous. Hence, the elastic softening of Si appears to be a consequence of amorphization. Moreover, it was observed quantitatively that the thermally activated shear viscosity of amorphous silicon at room temperature ($10^{17} N s m^{-2}$) was four orders of magnitude larger than that of irradiated Si [Volkert 91]. The low viscosity in the presence of ion beam is the reason for mass flow after incubation fluence required for amorphization.

4.5.6 Density modification vs lateral mass transport

In semiconductor materials, irradiation causes density change. For example InP compacts when irradiated by ions [Cliché 94]. In its relaxed state amorphous InP is found to be 0.17% more dense than crystalline InP. Whereas, the density of ion induced amorphous Si is found to be 1.8% less than the crystalline Si [Custer 94]. This effect is very different from the lateral mass transport effect. In our observations, we found that dike or step structures are separated from ditch. This means that lateral mass transport completely overshadows this effect.
4.5.7 Is lateral mass transport really a boundary effect?

We observed that the mass transport on the surface is not only limited to the boundaries between the irradiated and non-irradiated zones. It is inhomogeneously distributed over the irradiated surfaces. In case of Si, it is found in the form of ditch and dike structures. The formation of these structures is understood in terms of the fluctuations in the a/c interface, which act like an internal mask. Whereas, in InP the mass transport was observed at the external steel mask boundary separating irradiated and unirradiated zones. Hence, LMT is really a boundary effect, where the stress can relax.

4.5.8 Lateral mass transport is a low temperature phenomenon

These structures are visible only at low temperature (80 K). At high temperature (even at room temperature) mobile defects in the matter can lead to a relaxation, which may bring the material closer to its original undeformed state. However, the deformation could be frozen in by maintaining the temperature low enough to immobilize all defects produced during irradiation.

4.6 Power spectral density analysis

The surface RMS roughness is insufficient to give a full account of surface modifications. Since, it gives information along vertical direction and hence morphology parallel to surface plane is left out. Power spectral density (PSD) provides quantitative information about surface roughness both in vertical and lateral directions and is also independent of scan size. The PSD function is two dimension Fourier transform of the surface and is defined as [Petri 94]:

\[
r(r) = \frac{1}{\text{area}} \left| \iint \frac{dr}{2\pi} e^{-iqr} \langle h(r) \rangle \right|^2 ; r = (x,y) \quad \cdots (4.2)
\]

where \( q \) is the spatial frequency and \( h(r) \) is the height of the surface at position \( r \).

In present study data acquisition is done in constant force mode of AFM with 256 x 256 data points. The length scale considered in this study is 1 \( \mu m \), which gives sampling rate as 1 \( \mu m/256 \approx 3.9 \) nm. This corresponds to the spatial frequency ranging from \( q_{min} = \)}

\[ \]
Ion-beam-induced lateral mass transport

1/1\mu m = 1 \mu m^{-1} to q_{max} = 1/3.9nm \approx 256 \mu m^{-1} in reciprocal space. But for 2D isotropic PSD analysis, samples are taken from image center and the sampling frequency is limited to N/2L, where N is the scan size in pixels. This means that q_{max} = 256/2 \mu m^{-1} = 128 \mu m^{-1} as the maximum frequency. This forms the upper bandwidth limit of PSD plot.

The PSD curve of 200 MeV \textsuperscript{107}Ag\textsuperscript{+14} ion irradiated Si surface at fluence ranging from 10^{12} to 10^{14} ions cm\textsuperscript{-2} is shown in Figure 4.16. PSD curves are taken from the Fourier transform of AFM images having the trapezoid structures. For each of the curve, three parameters are of relevance: (1) the plateau height value W_{o}, which is related to the height of the rough surface, (2) the correlation length \xi_{o}, which defines the lateral extent of the surface roughness, and (3) the behavior at large q, which gives the nature of the roughness. The surface corrugation may be defined as the slope of a line connecting two points on the surface. Corrugation becomes small for points separated by a length larger than the correlation length \xi_{o}. For length larger than \xi_{o}, the surface can be considered as flat. Thus, it is expected that the PSD function should be q independent for q<q_{o}, while it should decrease for q>q_{o} [Eklund 93]. At q>q_{o}, no special value of spatial frequency q is the characteristic of the surface morphology and the PSD curve displays power law dependence.

\[ \gamma = Aq^{-n} \]  

where q is the spatial frequency, A is a constant and n is a real number. This shows the self-affine fractal properties of the surface after ion bombardment [Krim 93]. The fractal dimension D and scaling factor H can be deduced from the power law dependence of PSD function \gamma with spatial frequency q. The fractal dimension D, power law exponent n and scaling factor H with varying fluences are given in Table 4.2.

<table>
<thead>
<tr>
<th>Fluence (ions cm\textsuperscript{-2})</th>
<th>N</th>
<th>H</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 \times 10^{12}</td>
<td>2.9</td>
<td>0.45</td>
<td>2.55</td>
</tr>
<tr>
<td>1 \times 10^{13}</td>
<td>3.5</td>
<td>0.75</td>
<td>2.25</td>
</tr>
<tr>
<td>5 \times 10^{13}</td>
<td>3.7</td>
<td>0.85</td>
<td>2.15</td>
</tr>
<tr>
<td>5 \times 10^{13}</td>
<td>3.9</td>
<td>0.95</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 4.2 The power exponent n, scaling factor H and fractal dimension D of 200 MeV Ag\textsuperscript{+14} ions irradiated Si(111) surfaces as a function of fluence.
The fractal dimension $D$ lies between 2 and 3. The fractal dimension 2 means the plane surface (roughness can be thought as introducing third dimension). It decreases from 2.55 at a fluence of $5 \times 10^{12}$ ions cm$^{-2}$ to 2.05 at the fluence of $10^{14}$ ions cm$^{-2}$. This reduction in fractal dimension indicates the smoothing of the irradiated surface at $10^{14}$ ions cm$^{-2}$ fluence. The slope of the PSD tail (for $q > q_o$) evolves as $q^{-2.9}$ for fluence of $5 \times 10^{12}$ ions cm$^{-2}$ and becomes $q^{-3.9}$ for $10^{14}$ ions cm$^{-2}$ fluence. Moreover, larger the magnitude of PSD function larger is the perturbations on the surface. From Figure 4.16, it is observed that correlation length remains approximately constant for all fluences used. The plateau height $W_o$ increases from $67.0 \times 10^4$ A$^4$ at $5 \times 10^{12}$ ions cm$^{-2}$ to $1.7 \times 10^5$ A$^4$ at $5 \times 10^{13}$ ions cm$^{-2}$ fluence and then decreases to $6.2 \times 10^3$ A$^4$ at $10^{14}$ ions cm$^{-2}$.

Before overlapping of the damaged regions one can use the stochastic approach by introducing shot noise in the ion fluence and damage cross section can be determined by the use of Poisson’s formula. After the overlapping of the damaged zones i.e. a critical fluence $\phi_c$ the pure stochastic process needs to be modified because the cumulative effects due to the interaction of damaged zones may lead to the formation of correlated structures on the SHI irradiated surface. PSD analysis reveals the correlated structures since it expresses roughness in the reciprocal space. The general behavior of correlation function for ion bombarded surfaces is different from either the random or the periodic surface. Theoretical studies of non-equilibrium growth of interfaces indicate that correlation resulting from random events is possible [Kardar 86]. Eklund et al. quantitatively studied the Ar sputtered graphite surfaces by STM [Eklund 91]. The general form of the continuum differential equation describing the surface profile as a function of space and time is given as:

$$\frac{\partial h}{\partial t} + D_s \nabla^4 h - D_v \nabla^3 h - \chi \nabla^2 h - J \theta(h) + \eta(r,t)$$  \hspace{1cm} (4.4)

where $D_s$ and $D_v$ are the surface diffusion and volume diffusion coefficients, $\chi$ contains a constant characteristic of the material, $\eta(r,t)$ is the shot noise term in incident ions, $\theta$ is the term proportional to the sputter removal and $J$ is the incident flux. The resulting reciprocal space correlation function is given as:

$$\langle |h(q)|^2 \rangle, \alpha - \frac{J}{\omega(q)} \left[ 1 - e^{-\omega(q)\xi} \right]$$  \hspace{1cm} (4.5)
where $\alpha(q)$ is the healing rate of surface modulation of wave vector $q$. According to the equation 4.5 for small $q$ values, $\langle |h(q)|^2 \rangle$, is independent of $q$, while for large $q$ it should decrease with increase in $q$. This indicates two distinct regions in plot of $\langle |h(q)|^2 \rangle$, versus $q$, which is observed experimentally as shown in Figure 4.16.

At high fluence ($\geq 10^{13}$ ions cm$^{-2}$) the ion impacts with surface will have closer space separation, which enhances the surface diffusion and effectively smoothened out the roughness. For large fluence and $q\gg 0$, the exponential term can be neglected making $\langle |h(q)|^2 \rangle$, independent of fluence. However, Figure 4.16 indicates a significant fluence dependence of $\langle |h(q)|^2 \rangle$, at large wave vector.

Eklund et al. studied the height correlation function variation with temperature and found that $\langle |h(q)|^2 \rangle$, has a $q^{-4}$ dependence for large wave vectors, which demonstrate that surface diffusion dominates at higher temperatures [Eklund 93]. Ion impacts on the surface may cause localized heating. Based on thermal spike model the local increase in temperature caused by 5 keV Ar ion with surface indicate temperature of $\sim 660$ K in the vicinity of an impact site [Eklund 93].

![Figure 4.16](image)

**Figure 4.16** Plots of power spectral density function $\gamma$ versus spatial frequency $q$ for 200 MeV Ag$^{14}$ ions irradiated Si(111). The curves corresponding to the fluences of (a) $5 \times 10^{12}$ (filled triangle up), (b) $10^{13}$ (open diamond), (c) $5 \times 10^{13}$ (open circle), and (e) $10^{14}$ ions cm$^{-2}$ (open triangle down) respectively are shown. A $1/q^4$ dependence is shown for large spatial frequency for comparison.
Hence, PSD analysis of the irradiated surface indicates enhanced surface diffusion process on the surface. This causes lateral mass transport on the irradiated surface, which is analyzed by AFM topography in real space. The roughening mechanism other than shot noise in the fluence like dangling bonds induced surface roughening has been considered [Singh 2000c].

4.7 Possibility of artifacts

It is very important to justify lateral mass transport process, as it is not an artifact. The possibility of surface evaporation for ditch formation is very small in present case because each ditch is associated with a dike structure consisting of a large and a small dike on both side of the ditch (see Figure 4.5). Further the area of ditch is equal to the areas of dikes on the surface within 16% error. One alternative explanation of presently observed ditch and dike structures may be due to sputtering at ditch and accumulation of the sputtered atoms on dike through surface diffusion. The sputtering yield at MeV energy is very small ($4.5 \times 10^{-2}$ atoms/ion as estimated from SRIM-98 [Ziegler 85]) for 200 MeV Ag ions irradiation on Si. The maximum erosion after $5 \times 10^{13}$ ions cm$^{-2}$ fluence and at this sputtering yield is only 0.8% of a monolayer, whereas the observed ditch is 250 Å deep. Moreover, the surface diffusion would be more effective at room temperature than at liquid nitrogen temperature [Chason 94].